The Vapor Pressure of Solutions of Potassium in Liquid Ammonia

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SUBMITTED TO THE GRADUATE FACULTY
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1930

BY
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THE VAPOR PRESSURE OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA*

BY WARREN C. JOHNSON AND ALBERT W. MEYER

It is essential that the vapor pressures of solutions of the alkali metals in liquid ammonia be known so that the true concentration of any solution may be readily determined in the various investigations of its physical properties. These vapor pressure measurements are required at several temperatures and over a considerable range of concentration. Data are available for solutions of sodium[1] dissolved in liquid ammonia at many different temperatures, and for solutions of lithium[2] at $-39.4°$. Joannis has measured the vapor pressures of saturated solutions of potassium in liquid ammonia at temperatures ranging from $-20°$ to $+40°$, and, in addition, has determined a few values of the vapor pressure of concentrated solutions of this metal at $0°$ and at $8.44°$.

The pressure-composition curve offers a means of determining the solubility of the alkali metal in liquid ammonia at any given temperature. When ammonia is added to the metal, the resulting solution shows a constant vapor pressure, that of the saturated solution, as long as any undissolved metal remains. The change in the vapor pressure in passing from the saturated solution to those less concentrated in metal is very abrupt. It is possible to obtain several points on the curve in this region by careful manipulation in the experimental procedure. When this curve is extrapolated to intersect the horizontal line representing the vapor pressure of the saturated solution, there is obtained a point corresponding to the composition of the saturated solution. By this procedure, Joannis has found that, at $0°$ and $8.44°$, 1 gram atom of potassium dissolves in 4.31 and 4.37 gram molecules of ammonia respectively. According to these values the solubility of potassium decreases as the temperature is increased from $0°$ to $8.44°$. Since he records only two values at $0°$ at concentrations less than saturation, it is quite probable that the extrapolation he made to determine the solubility is considerably in error.

Ruff and Geisel[3] have determined the solubility of potassium in liquid ammonia by an entirely independent method. An amount of ammonia, insufficient to dissolve all the metal, was added to metallic potassium in small tubes. Above the mixtures was placed some cotton wadding and the upper end of the tubes was sealed. The tubes containing the material were then agitated for three hours to insure saturation. After this period they were

* Contribution from the Kent Chemical Laboratory of the University of Chicago.

[1] Joannis: Ann. Chim., (8) **7**, 5 (1906); Kraus, Carney and Johnson: J. Am. Chem. Soc., **49**, 2206 (1927).

[2] Kraus and Johnson: J. Am. Chem. Soc., **47**, 725 (1925).

[3] Ruff and Geisel: Ber., **39**, 831 (1906).

inverted to allow the solution to filter through the wadding. When an amount sufficient for analysis had filtered, the tubes were immediately placed in a Dewar flask containing liquid air, in order to freeze the entire contents. Then the bottom part of each tube was broken off immediately above the saturated solution without allowing the contents to melt. The solution was finally analyzed according to the usual procedures. These investigators used this method to prepare and analyze saturated solutions of potassium in liquid ammonia. At 0°, −50° and −100° the composition of the saturated solutions was found to be 4.74, 4.79 and 4.82 gram molecules of ammonia respectively per gram atom of potassium. According to these values the solubility of potassium in liquid ammonia increases slightly with increasing temperature over the range from −100° to 0°.

Kraus and Lucasse[1] were able to determine the composition of a saturated solution of potassium in liquid ammonia by measuring the specific conductance as a function of the concentration. They found that at −33.5° one gram atom of potassium is dissolved in 4.87 gram molecules of ammonia.

The present investigation was undertaken to determine the vapor pressures of solution of potassium dissolved in liquid ammonia at various concentrations at the temperatures, 0°, −33.5° and −50.38°. The solubility of potassium in ammonia is obtained from the data.

Experimental Part

The apparatus was so designed that the vapor pressures could be readily determined for a series of concentrations ranging from that of a saturated solution to one quite dilute in dissolved metal. The method employed was essentially the same as that used by Kraus and Johnson in their measurements with lithium solutions. A soda-glass tube approximately 30 mm. in diameter, having a total capacity of about 150 cc., served as a container for the solutions. A glass stirrer supported by a Chromel wire spring, which was hung inside the tube, was used to agitate the solutions in order to facilitate the establishment of equilibrium conditions. The stirrer contained a cylindrical iron core which was actuated by passing an intermittent current through an external solenoid. The pressure was measured by means of a mercury manometer back of which was placed coordinate paper graduated in millimeters and mounted on a steel plate.

The ammonia introduced was measured in pipet cells graduated in 0.01 cc. and the manipulation was carried out according to the method of Kraus.[2] The volumes of the entire pipet system, of the lines leading to the manometers, and of the connecting tubes were determined by allowing ammonia gas to expand from a known volume and pressure into these various parts of the apparatus, the pressure being observed after each successive expansion. Fairly accurate values of these volumes were necessary in order that corrections might be applied for the amount of ammonia present in the vapor

[1] Kraus and Lucasse: J. Am. Chem. Soc., **43**, 2529 (1921).

[2] Kraus: J. Am. Chem. Soc., **43**, 749 (1921).

state after each introduction of liquid ammonia from the pipet cells, and for the amount of vapor between the solution and the manometer after equilibrium has been established.

The metallic potassium was introduced into the tube through a fine capillary according to the method of Kraus and Lucasse.[1] As soon as the capillary was sealed off, the vapor-pressure tube and the pipet lines were exhausted by means of a mercury vapor pump supported by a Hy-Vac oil pump. A measured amount of ammonia was then introduced from a pipet cell and solution of the metal was accelerated by putting the stirrer into operation. After the solution had been agitated for several minutes and the vapor pressure appeared to be constant, the manometer reading was noted, a small amount of ammonia vapor was withdrawn, and the pressure was again observed. In this manner equilibrium was approached from both sides and the procedure served as a means for determining true equilibrium pressures.

In order to withdraw ammonia, the vapor-pressure tube was connected to a larger tube having a capacity of 550 cc. which in turn was connected to a second manometer. When an amount of ammonia more than sufficient for saturation had been added to the potassium, the vapor above the solution was allowed to expand into the large reservoir, the pressure was observed on the second manometer and the solution was allowed to come to equilibrium again. The ammonia gas was then pumped out of the reservoir, the vapor pressure of the solution was noted, and the above process for withdrawing additional ammonia was repeated. This procedure was followed until the vapor pressure of the solution reached that of the saturated solution, thus enabling one to obtain several pressure readings in the more concentrated regions. The amount of ammonia withdrawn in each instance was determined by noting the temperature, volume and pressure, and the corresponding value was deducted from the total amount of ammonia present in order to obtain the true concentration of the solution. The process of withdrawing ammonia gas also served to remove small amounts of hydrogen that were present due to the formation of potassium amide. Although the amount of hydrogen formed in this reaction between ammonia and potassium was not great when the metal was free from its oxide, nevertheless, it was sufficient to produce a noticeable effect upon the total pressure readings in the highly concentrated solutions.

The measurements were carried out at three different temperatures, 0°, $-33.5°$ and $-50.38°$. To maintain the temperature at 0°, the vapor-pressure tube was surrounded by a Pyrex Dewar flask containing finely-chipped ice in equilibrium with water. A thermometer calibrated by the Bureau of Standards was inserted into the bath and it was noted that the temperature remained at $0° \pm 0.05°$ for a period of several hours. A thin-walled tube was placed around the vapor-pressure tube in order to keep the potassium away from the ice-water mixture in case of accident.

[1] Kraus and Lucasse: J. Am. Chem. Soc., **43**, 2529 (1921).

It was found more difficult to maintain constant temperature at the boiling point of liquid ammonia. The ammonia in the Dewar bath was allowed to boil against the atmosphere and the height of the liquid was kept as constant as possible by frequent additions. The atmospheric pressure was noted at frequent intervals during a determination. The variation in the temperature during a period of several hours was not greater than 0.1° under these conditions. The temperature was determined by noting at the beginning of a run the vapor pressure of pure liquid ammonia under the conditions to be followed in the course of the series of the measurements. The temperature corresponding to this pressure was then obtained from the tables given by Cragoe, Meyers and Taylor.[1] Four runs were carried out at the boiling point of liquid ammonia. The pressure of pure ammonia was measured in each case and found to be 755.0 mm., 754.4 mm., 752.8 mm. and 755.4 mm. respectively. The average value of these pressures corresponds to that of pure ammonia at a temperature of −33.5°. At this temperature the vapor pressure of pure ammonia changes approximately 38 mm. per degree; accordingly, the maximum variation in the temperature, as represented by the above pressures, is about 0.07°.

At −50° the temperature was controlled readily by boiling the ammonia in the Dewar bath under reduced pressure. An alcohol thermometer was placed in the bath, and, while a slow stream of hydrogen gas was allowed to bubble through the liquid for the purpose of maintaining uniform temperature conditions, the ammonia vapor was drawn off by means of a water-jet pump. The rate of evaporation was regulated by a screw clamp. The true temperature of the bath was determined by observing the vapor pressure of pure liquid ammonia when the thermometer reading was −50°. This pressure was found to be that of pure liquid ammonia at −50.38° according to the tables of Cragoe, Meyers and Taylor. The variation in the temperature throughout a series of measurements was not greater than 0.05°.

After a run had been carried out, the cooling bath was removed and the ammonia was allowed to escape. The potassium was then washed out of the vapor-pressure tube with ether, alcohol and, finally, water into a platinum dish. The greater part of the ether and alcohol was evaporated by warming and the alkaline solution was neutralized and acidified with hydrochloric acid. Finally, the solution was evaporated to dryness and the potassium chloride was heated to constant weight in a furnace at a temperature of 500°. The potassium was found to be free from iron and to contain only a minute amount of sodium. The ammonia used in the investigation was dried with metallic sodium and then distilled into a small steel cylinder.

Results

The results of four series of determinations at 0° are given in Table I; four series at −33.5° are given in Table II; and two series at −50.38° are given in Table III. The results obtained at 0° are plotted in Fig. 1, while

[1] Cragoe, Meyers and Taylor: Bur. of Standards, Sci. Pub., **369**, (1920).

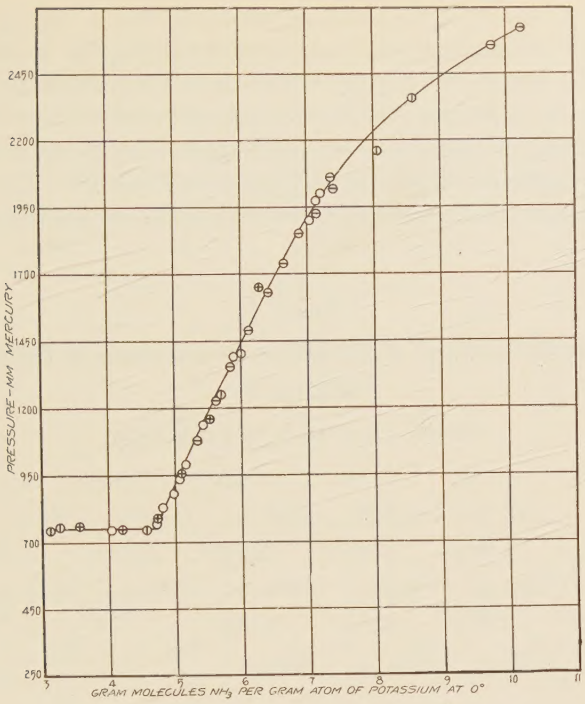
PRESSURE-MM MERCURY
2450
2200
1950
1700
1450
1200
950
700
450
250
3
4
5
6
7
8
9
10
11
GRAM MOLECULES NH3 PER GRAM ATOM OF POTASSIUM AT 0°

FIG. 1

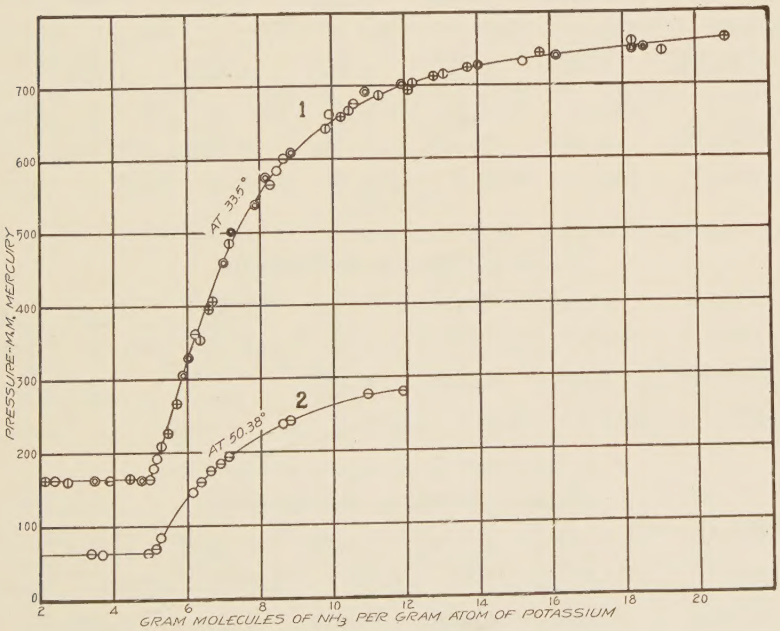
PRESSURE-M.M. MERCURY
700
600
500
400
300
200
100
0
2
4
6
8
10
12
14
16
18
20
1
AT 33.5°
2
AT 50.38°
GRAM MOLECULES OF NH3 PER GRAM ATOM OF POTASSIUM

FIG. 2

those at the two lower temperatures are shown in Fig. 2. Many of the values are not plotted, especially in the concentrated regions, due to the overlapping of points. The concentrations are expressed in gram molecules of ammonia per gram atom of potassium; the pressures are given in millimeters of mercury.

The solubility of potassium in liquid ammonia, as determined by the extrapolation method outlined above, is given in Table IV. The values found by Joannis, Kraus and Lucasse and Ruff and Geisel are likewise listed in this table.

TABLE I

Vapor Pressure of Solutions of Potassium in Ammonia at Different Concentrations at 0°

Series 1, 1.2818 g. of Potassium

Conc. NH_3/K	1.145	2.542	4.030	5.409	5.332	5.243
Press., mm.	748.3	755.9	748.9	1140.2	1082.5	1005.4
Conc. NH_3/K	5.147	5.050	4.956	4.701	4.615	5.880
Press., mm.	992.9	937.4	884.8	769.9	741.9	1393.6
Conc. NH_3/K	5.831	7.201	7.041			
Press., mm.	1356.1	2001.4	1901.9			

Series 2, 0.2806 g. of Potassium

Conc. NH_3/K	4.056	3.950	7.357	7.141	6.880	6.416
Press., mm.	799.5	753.3	2062.2	1975.1	1854.0	1632.0
Conc. NH_3/K	6.113	5.883	5.615	5.347	5.082	4.800
Press., mm.	1491.7	1354.9	1229.9	1091.2	965.2	832.8
Conc. NH_3/K	4.561	7.410	7.137	6.644	10.225	9.776
Press., mm.	760.1	2018.2	1927.6	1740.9	2623.4	2557.7

Series 3, 0.6501 g. of Potassium

Conc. NH_3/K	3.555	6.226	6.089	5.868	5.519	5.094
Press., mm.	764.4	1651.6	1501.5	1398.3	1161.5	959.2
Conc. NH_3/K	4.806	4.708	4.188			
Press., mm.	835.5	792.6	750.4			

Series 4, 0.4588 g. of Potassium

Cons. NH_3/K	3.260	3.123	5.999	5.692	5.394	5.098
Press., mm.	760.8	747.1	1405.7	1226.9	1070.7	918.3
Conc. NH_3/K	4.779	4.549	8.594	8.061	7.466	
Press., mm.	808.2	748.9	2360.5	2161.2	2018.8	

TABLE II

Vapor Pressure of Solutions of Potassium in Ammonia at Different Concentrations at $-33.5°$

Series 1, 1.9412 g. of Potassium

Conc. NH_3/K	1.657	2.745	3.900	5.272	5.177	5.082
Press., mm.	165.0	163.5	167.0	208.0	191.0	177.2
Conc. NH_3/K	5.009	4.946	8.639	8.434		
Press., mm.	166.0	162.2	599.5	583.5		

Series 2, 1.5144 g. of Potassium

Conc. NH_3/K	2.386	3.773	3.695	5.188	5.084	4.984
Press., mm.	162.0	161.0	161.0	202.8	186.5	172.8
Conc. NH_3/K	4.877	6.193	8.431	8.274	10.576	10.437
Press., mm.	162.0	359.6	571.4	564.6	675.2	669.8
Conc. NH_3/K	13.077	12.470	15.231			
Press., mm.	722.5	707.2	732.3			

Series 3, 1.7333 g. of Potassium

Conc. NH_3/K	1.887	2.725	3.636	4.574	5.504	6.238
Press., mm.	159.7	159.5	161.6	166.2	294.5	396.2
Conc. NH_3/K	7.181	8.031	8.822	8.696	9.806	10.457
Press., mm.	500.3	566.9	615.0	601.2	640.5	666.3
Conc. NH_3/K	11.280	12.221	13.069	13.977	19.079	
Press., mm.	686.0	703.0	714.0	722.2	745.0	

Series 4, 0.8829 g. of Potassium

Conc. NH_3/K	2.134	4.429	6.581	6.331	6.007	5.714
Press., mm.	162.1	162.8	393.6	351.7	309.7	265.1
Conc. NH_3/K	5.462	5.248	5.067	4.899	6.682	8.352
Press., mm.	226.4	193.7	168.7	161.0	405.0	561.3
Conc. NH_3/K	10.228	12.792	12.096			
Press., mm.	657.4	711.8	693.6			

TABLE III

Vapor Pressure of Solutions of Potassium in Ammonia at Different Concentrations at $-50.38°$

Series 1, 1.1405 g. of Potassium

Conc. NH_3/K	1.485	3.686	5.269	5.200	5.131	5.062
Press., mm.	62.9	61.8	83.6	76.3	72.0	67.5
Conc. NH_3/K	5.006	6.895	8.801	8.609	10.264	11.900
Press., mm.	62.6	183.9	240.9	236.6	258.0	278.3

Series 2, 1.2304 g. of Potassium

Conc. NH_3/K	1.647	3.390	4.983	4.932	6.626	6.496
Press., mm.	63.4	63.5	64.8	62.6	174.4	166.4
Conc. NH_3/K	6.372	6.254	6.139	5.319	5.257	5.196
Press., mm.	159.1	152.3	145.2	81.2	76.6	72.0
Conc. NH_3/K	5.140	5.086	5.036	7.128	7.036	10.942
Press., mm.	68.7	64.6	63.6	193.2	187.9	276.5

TABLE IV

Solubility of Potassium in Liquid Ammonia

Temperature	0°	−33.5°	−50.0°	−100°
Johnson and Meyer	4.68	4.95	5.05	——
Joannis	4.31	——	——	——
Ruff and Geisel	4.74	——	4.79	4.82
Kraus and Lucasse	——	4.87	——	——

Discussion

The form of the vapor pressure curves for potassium dissolved in liquid ammonia corresponds closely to that of the curves for sodium and lithium. The vapor pressure of the solutions remains fixed as long as any potassium is present in equilibrium with the saturated solution. When solution of the potassium is complete, a marked increase in the vapor pressure is noticed as the concentration decreases. At still lower concentrations, the curves flatten out and approach the vapor pressure of pure liquid ammonia at the temperature in question. There are no breaks in the curve to indicate the formation of a compound between potassium and ammonia.

It will be noticed that the data given for the saturated solutions are not entirely consistent. This is due to the fact that in many instances the solutions were not allowed to come to equilibrium after each addition of ammonia, since, at these high concentrations, considerable time is required to establish true equilibrium conditions. The vapor pressure of the saturated solution was determined at each temperature independently and was found to have a value of 750 mm. at 0°, 162 mm. at −33.5° and 63 mm. at −50.38°. The first value is in agreement with that found by Joannis at 0°.

The data appear to be somewhat inconsistent at high concentrations where the curves are very steep. This is especially true at 0°. At this temperature, the vapor pressure changes approximately 250 mm. for a change in concentration of only 0.5 gram molecules of ammonia per gram atom of potassium. Hence, an appreciable change in pressure corresponds to a very small difference in concentration.

It is evident from the data given in Table IV that the solubility of potassium in liquid ammonia increases slightly with increasing temperature from −50.38° to 0°. At −50.38°, 100 grams of liquid ammonia dissolves 45.56 grams of potassium; at −33.5°, 46.38 grams of potassium; and at 0°, 49.05 grams of potassium. Ruff and Geisel also found that the solubility increases slightly with the temperature. The value given by these investigators for the composition of the saturated solution at 0° is 4.74 gram molecules of ammonia per gram atom of potassium, which is in good agreement with our value of 4.68. At −50°, the discrepancy in the results is much greater. It would appear that the value of 4.31 gram molecules of ammonia per gram atom of potassium given by Joannis at 0° is in error. Since he determined only two points at concentrations lower than that of saturation, it is difficult to conceive of an extrapolation possessing any significance.

Summary

The vapor pressures of solutions of potassium in liquid ammonia have been measured at 0°, −33.5° and −50.38° over a considerable concentration range.

The vapor pressures of the saturated solutions of potassium in ammonia at these temperatures are 750 mm., 162 mm. and 63 mm., respectively.

The solubility of potassium in liquid ammonia increases slightly with increasing temperature from −50.38° to 0°. The composition of the saturated solution, expressed in gram molecules of ammonia per gram atom of potassium, is 4.68 at 0°, 4.95 at −33.5 and 5.05 at −50.38°.

There is no evidence for the formation of a compound between potassium and ammonia.